NON-FUEL USES OF COALS AND SYNTHESIS OF CHEMICALS AND MATERIALS

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ABSTRACT

This paper provides an account of our analysis of future needs for non-fuel uses of fossil fuels, particularly coal, and a discussion of possible routes for developing chemicals and materials. An overview of energy supply and demand in the world and the existing non-fuel uses of fossil fuels in the U.S. will be given first. The amount of energy used for non-fuel purpose is small compared with the amount of energy consumed by end users. Nevertheless, the non-fuel uses of fossil fuels may become more important in the future. The demonstrated coal reserves in the world are enough for consumption of over 220 years at the 1992 level, while the oil reserves are only about 40 times of the world's consumption level in 1992. Coal may become more important both as energy source and as the source of chemical feedstocks as we move into the 21st century. However, traditional non-fuel uses of coals (coke ovens and the coal tars) are diminishing rapidly. We will discuss the possible new processes for making both bulk and specialty chemicals and polymers and carbon materials from coals and liquids from coal liquefaction. Specific examples will be provided from work in progress in our laboratory, including conversion of coals and coal liquids to specialty chemicals, polymer materials, activated carbons, graphitic carbons, and electrode materials.

WORLD AND U.S. SUPPLY AND DEMAND OF FOSSIL FUELS

Table 1 summarizes energy supply and demand in the world and in the U.S., and the U.S. primary energy input into the electric utilities. The energy statistics data in this paper were derived from several recent DOE/EIA reports [EIA AER, 1993; AEO, 1994; IEO, 1994; IPSO, 1994; MER, 1993; QCR, 1994]. Fossil fuels are the dominant sources of energies for modern societies as well as chemicals and synthetic organic materials.

Currently the world consumes 66.9 million barrels of oils per day (mbpd) and 24.34 billion barrels per year (136.3 quadrillion Btu/year). According to the most recent report, the estimated crude oil reserves in the world are 999.1 billion barrels, with 66.3% in the Middle East region but only about 2.4% in the U.S. The world is consuming petroleum at a very fast speed. The sum of all the petroleum reserves in world is only 41 times the consumption in 1992.

As of 1992, the sum of all the known natural gas reserves in the world is 4375.8 trillion cubic feet, with about 40% in the former Soviet Union and only 3.8% in the U.S. The world total consumption in 1992 reached 74.7 trillion cubic feet, which is equivalent to 74.3 quadrillion Btu. The known reserves in the world are about 59 times the consumption level in 1992.

The worldwide coal consumption in 1992 is 5001 million short tons (4535.9 million metric tons), which is equivalent to 88.9 quadrillion Btu. The world coal reserves are 1145.3 billion short tons (1038.5 billion metric tons), with about 23.1% in the U.S. The world coal reserves are over 225 times the consumption level in 1992. In particular, coal is the most abundant fossil hydrocarbon resource in the U.S., and the U.S. coal reserves (265.2 billion short tons) are about 300 times the current domestic annual consumption. Coal is expected to become more important in the future both as energy source and as the source of chemical feedstocks.

OVERVIEW OF NON-FUEL USES OF FOSSIL FUELS

Table 2 shows the amount of fossil hydrocarbon resources used for non-fuel purposes. Non-fuel use of fossil fuels in the U.S. is small compared with the amount of energy consumed as fuels by end users. As shown in Table 2, the non-fuel use of fossil resources is overwhelmingly the use of petroleum products, primarily petrochemical feedstocks, asphalt and road oil, petroleum coke, and liquefied petroleum gases. Non-fuel use of coal is dominated by the coal carbonization to make metallurgical coke. The non-fuel use of natural gas includes making synthesis gas, olefins, and carbon blacks. In 1992, the 5.84 quadrillion Btu consumed for non-fuel uses of fossil fuels (including coals for coke production) represented 7.1% of total energy consumption in the U.S. (82.42 quadrillion Btu). Non-fuel use of petroleum is 13.2% of petroleum consumed in the U.S.

Status of U.S. Coal Production and Utilization. Figure 1 shows the profile of the U.S. coal production by type over the period 1960-1992. Currently U.S. coal industry employs about 120 thousand miners, and produces about 1 billion short tons (about 900 million metric tons) of coals annually [NCA, 1993]. About 90% of the coals are consumed domestically. About 10% of coals mined in the U.S. are exported, and they are bituminous coals, including about 43 and 60 million short tons of steam coals and metallurgical coals, respectively [NCA 1993].

As shown Table 3, electric utilities are the dominant consumers of coals. In fact, their consumption grew from 177 to 780 million tons during 1960-1992 [Song, Schobert, Scaroni, 1994]. The percentage distribution of the domestic consumption in 1992 is as follows: 87.2% by utilities, 8.4% by industries, 3.8% by coke plants, and 0.6% by residential and commercial users. Coal accounted for about 80 % of all the fossil fuels consumed at electric utilities in 1992.

Non-fuel Uses of Coals. Existing non-fuel uses of coals include (1) high temperature carbonization of bituminous coal to make metallurgical coke; (2) gasification of coal to make synthesis gases and other chemicals; (3) use of coal in manufacturing other materials such as activated carbons, carbon molecular sieves (CMS) and production of phosphoric acid; (4) the use of coal tars from carbonization (and gasification) for making aromatic chemicals; and (5) the use of coal tar pitch for making carbon fibers and activated carbon fibers, and other related products.

Energy Policy Act of 1992. Non-fuel uses of coals have also been described under the Section 1304 of the National Energy Policy Act of 1992: The Secretary of Energy shall plan and carry out a program of research, development, demonstration, and commercial application with respect to technologies for the non-fuel use of coal, including (1) production of coke and other carbon products derived from coal; (2) production of coal-derived, carbon-based chemical intermediates that are precursors of value-added chemicals and polymers; (3) production of chemical feedstocks via coal treatment processes.

Non-fuel Use through Coal Liquefaction. It is expected that coal liquefaction could become a viable option sometime in the next century, for producing liquid transportation fuels as well as chemical feedstocks. Despite enormous strides in coal liquefaction research and development, coal-derived liquid fuels are still not economically competitive with petroleum. However, the economic analysis of the viability of coal liquefaction may well produce a different result if some coal-derived liquids, particularly aromatic and phenolic compounds, can be used for making value-added chemicals and polymer materials. Just as crude oils are also used for making petrochemicals, the liquids from coal liquefaction are expected to provide the needed organic chemicals, albeit in smaller amounts compared to their use as fuels.

The importance of promoting non-fuel uses of coal in conjunction with coal liquefaction in the future is also apparent from the following facts. In 1970 the daily petroleum production and consumption in the U.S. were 9.64 and 14.70 million barrels, respectively. However, the U.S. petroleum production decreased to 6.84 million barrels/day in 1993, whereas the consumption increased to 17.03 million barrels/day. The worldwide petroleum consumption also rose from 46.81 million barrels/day in 1970 to 66.93 million barrels/day in 1993, which is a 43% increase in 22 years. Currently, the U.S. petroleum consumption is about 24.6% of the world's total consumption, but U.S.'s petroleum reserves are only about 2.4% of the world's total reserves. The remaining crude oils in the existing reserves are getting heavier. For example, the average API gravity of crudes refined in the U.S. decreased from 33.8 to 31.8 during the 10 years between 1980 and 1990; related to this increase in density (decrease in API gravity) is a constant rise in the sulfur content of the crude oils, from 0.88 wt% in 1980 to 1.11 wt% in 1990 [Swain, 1991]. With the continuing decline in the resource and in the quality of crude oils, the processing of coal-derived oils in existing petroleum refineries may become economically viable sometime in the 21st century.

Liquids from coal liquefaction may be used as feedstocks for making organic chemicals and various carbon materials, in addition to their use for producing transportation fuels. Relative to heavy oils, the problems associated with refining coal-derived liquids are their higher contents of aromatics, particularly polycyclic aromatics, and higher contents of nitrogen- and oxygen-containing compounds. Sulfur removal does not seem to be such a technical problem, since it is thought that hydrodesulfurization is easier, chemically, than hydrodenitrogenation. In the context of the production of chemicals and specialty materials, however, the high contents of aromatics, phenolics, and nitrogen compounds may provide a practical application of the folk adage, "If life hands you a lemon, make lemonade." If the "lemon" is the problem of dealing with the oxygen and nitrogen compounds prior to conventional refining for fuel use, the "lemonade" may be the use of these compounds and their derivatives for making value-added chemicals and monomers for aromatic polymer materials.

SYNTHESIS OF CHEMICALS AND POLYMERS FROM COALS

Before 1945 about 75% of all the organic chemicals in the world were based on coal-derived liquids, but with the advent of vast petroleum resources in the world during the 1940s, crude oil gradually became dominant chemical feedstocks by 1960. Currently petroleum and natural gas account for more than 90% of the major industrial organic chemicals [Speight, 1991; Sheldon, 1983]. These resources are the primary sources of the seven basic organic chemical building blocks: ethylene, propylene, butadiene, benzene, toluene, the xylenes, and methanol. However, coal tars remain an important source of aromatic chemicals. The annual consumption of aromatic chemicals worldwide is about 25 Mt for benzene, toluene, and xylenes; and 5 Mt for naphthalene and three- and four-ring compounds [Murakami, 1987; Collin, 1985]. Coal tar accounts for about 15–25% of the BTX production and 95% of the larger aromatics.

The last two decades have witnessed enormous developments in various organic and carbon-based materials [Song and Schobert, 1993], and it is certain that the late 1990's and the 21st century will see significant further growth of these materials. Examples include engineering plastics, liquid crystalline polymers, high-temperature heat-resistant polymers, polymer membranes, graphitic carbon materials, carbon fibers, and activated carbon fibers. Many of the starting materials for monomers of the aromatic polymer materials are not readily available from petroleum.

Scheme I shows some important aromatic polymer materials [Song and Schobert, 1993]. Scheme II gives the structures of some important liquid crystalline polymers [Song and Schobert, 1993]. Due to the recent development of many aromatic polymer materials, there is a great demand for aromatic monomers. Since the U.S. production of coal tar, which is an important source for 1- to 4-ring chemicals (particularly 2- to 4-ring aromatics), has declined significantly in the past decade, there is a need for developing an alternative source of aromatic chemicals in the future. With the rapidly increasing engineering applications of aromatic compounds for polymer materials, the demands for many aromatics of one to four rings have increased in the recent past, and this trend is expected to continue into the 21st century. Thus an excellent opportunity exists to explore the potentials of developing value-added chemicals and specialty materials from coals and the liquids obtained from coal liquefaction.

As we have discussed in detail elsewhere [Song and Schobert, 1993], research on deriving coal-based chemicals from coal liquids can be viewed as an extension of coal liquefaction research. Development of value-added chemical products could both increase the economic viability of coal liquefaction and make coal liquids more competitive with petroleum because coal liquids contain many compounds not found in petroleum [Song et al., 1991, 1992; Lai et al., 1992; Zhou et al., 1992; Saini and Song, 1994]. In analogous fashion, the economic viability of processing heavy residual materials could also be strengthened if approaches were developed for their conversion into value-added chemical feedstocks as well as transportation fuels.

We suggest that two broad approaches can be taken for coal conversion into value-added chemicals. The first can be viewed as the indirect approach, analogous to the so-called "indirect" coal-to-chemical conversion [Schobert, 1984]. The essence of the indirect approach would be the conversion of coals to liquids. Once the liquids were obtained, they would be subjected to appropriate separation or conversion operations to produce the chemical products of interest. However, separation of coal liquids into individual compounds is time consuming and expensive. An analogy from coal processing is the concept of combining short-contact-time liquefaction with catalytic dealkylation to produce aromatic hydrocarbon monomers [Song et al., 1989; Hirota et al., 1989]. The simplified aromatic compounds will then be used for making value-added products. The alternative, much bolder and of much higher risk, is the direct approach. In this approach a reagent would be introduced to the coals to cleave only a certain well-defined set of bonds and carefully cut out the molecular structures of interest. The highly selective removal of these structures could lead to monomers or precursors to the monomers for some of the high-performance polymer materials. An analogy proposed for direct production of chemicals from coal would be the use of selective oxidation to generate high yields of benzene carboxylic acids from low-rank coals [Song and Schobert, 1993].

On-going Research on Catalytic Synthesis of Chemicals in This Laboratory

In this section, specific examples will be provided from work in progress in our laboratory, including conversion of aromatic compounds in coal liquids to value-added chemicals, specialty chemicals, and monomers for polymer materials. We are exploring the catalysts, reactions, and processes for developing value-added chemicals and materials from coal-derived, carbon-based compounds.

Production of Phenol and Aromatics from Coals via Liquefaction. We are studying coal liquefaction in conjunction with the production of aromatic chemicals. Analysis of various coal-derived oils indicates that there are many 1- to 4-ring aromatic and polar compounds in coal-derived liquids that can be converted into valuable chemicals [Lai et al., 1992; Song and Schobert, 1993; Burgess et al., 1993; Huang et al., 1994; Saini and Song, 1994; Song and Saini, 1994; Lai and Song, 1995]. For example, phenol, naphthalene, and phenanthrene are rich in coal liquids from primary liquefaction of some coals. Phenol is one of the top twenty organic chemicals [CEN, 1994] and is commercially synthesized through multi-step process (benzene isopropylation, oxidation of isopropyl benzene, separation of phenol). However, phenol is rich in the oils from coal liquefaction, particularly when the liquefaction is promoted by dispersed catalysts and water [Song and Saini, 1994; Saini and Song, 1994]. Phenol can be separated directly from the coal liquids, and it can be used as or converted into monomer for many aromatic polymers and engineering plastics, including those shown in Scheme I. Naphthalene and its derivatives are rich in the oils from some bituminous coals. Naphthalene and 2-alkylnapthalene are important aromatic chemicals. It should be noted that the use of aromatic compounds, that are in coal liquids and heavy oils, for making value-added chemicals requires the starting material to be reasonably pure. Our recent catalytic studies include the shape-selective conversion of two- to three-ring aromatic compounds (naphthalene, phenanthrene, and their derivatives) into value-added chemicals, as described below.

Shape-selective Alkylation of Naphthalene. This catalytic reaction can produce 2,6-dialkyl substituted naphthalene (2,6-DAN). 2,6-DAN is needed now as the feedstock of monomer for making the advanced polyester materials such as polyethylene naphthalate (PEN, Scheme I), polybutylene naphthalate (PBN, Scheme I), and liquid crystalline polymers (LCP, Scheme II). By using some shape-selective catalysts, we have achieved selective alkylation of naphthalene, with over 65% selectivity to 2,6-DAN by using isopropanol [Song and Kirby, 1993, 1994] or propylene as the alkylating agent [Schmitz and Song, 1994]. We also found some simple and effective methods for enhancing the selectivity, which are not available in the prior arts [Schmitz and Song, 1994, unpublished data].

Ring-shift Isomerization of Phenanthrene Derivatives. This reaction leads to anthracene derivatives, particularly sym-octahydroanthracene (sym-OHAn). We have found that some catalysts selectively promotes the transformation of sym-octahydrophenanthrene into sym-OHAn, which we call ring-shift isomerization [Song and Moffatt, 1993, 1994]. Some catalysts can afford over 90% selectivity with high conversion [Lai and Song, 1994, unpublished data]. This work could provide a cheap route to making anthracene and its derivatives, which are valuable chemicals in demand, from phenanthrene, which is rich in coal tar from coal carbonization, pyrolysis, and liquefaction. Examples of the possible applications of sym-OHAn may include the manufacturing of anthracene (which is in demand for making dyestuffs), anthraquinone (which is an effective pulping agent), and pyromellitic dianhydride (which is the monomer for making polyimides such as Du Pont's Kapton).

Conformational Isomerization of cis-Decalin to trans-Decalin. The commercial decalin solvents are almost equimolar mixtures of cis-decalin and trans-decalin. In an earlier work using decalin as a solvent, we found accidentally that cis-decalin isomerize into trans-decalin at low temperatures (250°C) over some catalysts [Song and Moffatt, 1993, 1994], which would otherwise requires a high temperature such as 450°C [Song et al., 1992]. This work is a continuation of our earlier observation that trans-decalin has substantially higher thermal stability at high temperatures [Song et al., 1992]. Our recent experimental results indicate that it is possible to achieve over 90% conversion with 95% selectivity with some catalysts at low temperatures such as 200°C [Lai and Song, 1994, unpublished]. Possible application of this work is the manufacture of high-temperature heat-transfer fluids. Another application lies in the production of advanced thermally stable jet fuels, which can be used both as heat sinks and as fuels that are required for high-Mach aircraft [Schobert et al., 1994].

Shape-selective Naphthalene Hydrogenation. Complete hydrogenation of naphthalene in convential process produce mixtures of cis- and trans-decalin, and . In recent studies on naphthalene hydrogenation, we have found that certain catalysts selectively promote the formation of cis-decalin or trans-decalin [Song and Grainne, 1993, unpublished data; Schmitz and Song, 1994, unpublished data]. Now we can selectively produce cis-decalin, with over 80% selectivity at 100% conversion [Schmitz and Song, 1994, unpublished data]. cis-Decalin may have potential industrial application as the starting material for making sebacic acid, which can be used for manufacturing Nylon 6,10 and softeners.

PRODUCTION OF CARBON MATERIALS FROM COALS

Carbon materials represent an important market for non-fuel applications of coal and coal-derived pitch materials. We have discussed the possibilities of developing various coal-based carbon materials recently [Song and Schobert, 1993] based on the materials listed in several reviews by Walker [1986, 1990] and by Marsh [1989, 1991]:

- Metallurgical cokes
- Molecular sieving carbons (MSC)
- Pitch-based carbon fibers
- Mesocarbon microbeads (MCMB)
- Mesophase-based carbon fibers
- Carbon fiber reinforced plastic
- Carbon whiskers or filament
- Graphite and graphite-based materials
- Diamond-like films
- Activated carbons
- Activated carbon fibers
- Carbon electrodes
- Carbon blacks
- Intercalation Materials
- Elastic carbons
- Composite materials
- Fullerenes or "bucky-balls"

Carbon-based Materials Made Directly from Coals. Currently the production of metallurgical coke is the largest non-fuel use of coals, primarily bituminous coals. It is estimated that about 500 million tonnes (metric tons) of coke are produced annually in the world [Mochida and Sakanishi, 1993]. China is one of the largest producers and consumers of coals and coke. In 1992, China produced 1204 million short tons of coals [EIA IEO, 1994]. About 10% of coals mined in China are used for making metallurgical coke [Guo, 1994].

Figure 2 shows the profile of the U.S. metallurgical coal consumption and coke production over the period 1950-1992. Coal consumption by the U.S. coke industry (and some other industrial sectors) trended downward since early 1970s. The reasons have been discussed in our previous review [Song and Schobert, 1993]. In 1993, the metallurgical coal consumption and coke production in the U.S. were 31.3 and 23.2 million short tons, respectively. The annual demand for coke in the U.S. is expected to further decrease to 18.7 million short tons by 2002 [Gilbert, 1993]. The decrease in coke production also means a decline in coal tar production, which could lead to the shortage of both aromatic chemicals, particularly 2- to 4-ring chemicals, and the pitch feedstocks for making carbon fibers and other needed carbon materials. This also gives rise to the need for developing alternate coal-based feedstocks for making various aromatic chemicals and carbon materials.

Activated carbons are used mainly as adsorbents for liquid-phase and gas-phase applications. In 1992, the world total annual production of activated carbons from various feedstocks was estimated to be about 450,000 tonnes; among which 70,000 tonnes were produced in China, with about 30,000 tonnes made from coal and 40,000 tonnes from the other feedstocks [Gao, 1994]. The amount of coals used worldwide for producing activated carbons are estimated to be 200,000 tonnes/year [Golden, 1992]. Significant growth potential exists for this application, primarily for environmental protection, e.g., purification of water and air. Jagtoyen and Derbyshire have carried out a series of studies on the production of activated carbons from bituminous coals by chemical activation [Jagtoyen et al., 1992, 1993]. The liquid phase applications include water purification, decolorizing, food processing, and gold recovery, etc.; the gas phase applications cover air purification, gas treatment, and solvent recovery. More information on activated carbons may be found in a recent review by Derbyshire and co-workers [Derbyshire et al., 1994].

The amount of coals used worldwide for producing molecular sieving carbons are estimated to be 3,000 tonnes/year [Golden, 1992]. The application of molecular sieving carbons (MSC) for gas separation by pressure-swing adsorption (PSA) is now commercially viable. For example, MSC is used for air separation by Air Products and Chemicals Inc. It is expected that more companies will be engaged in producing MSC in the 1990's and into the next century.

The other industrial non-fuel uses of coals are included in those by industries and manufacturing plants, especially those who make chemicals, cement, paper, ceramics, and various metal products. Table 4 shows the U.S. coal consumption at manufacturing plants in 1992 by standard industrial classification (SIC) code [EIA QCR, 1994]. Use of coal for gasification can be partly classified as non-fuel use when the products are used as chemical feedstocks. Gasification is currently used for making synthesis gas ($CO + H_2$) and for producing H_2 for various hydrogenation and hydroprocessing in petrochemical and petroleum refining industries. The use of coal for gasification is included in Table 4 at the manufacturing plant with SIC code 29.

The details of the non-fuel uses at manufacturing plants are not available. However, direct coal injection into blast furnace is already in industrial practice. This use may have been included in SIC Code 33 in Table 4. There are some other interesting uses [Bonskowski, 1994]. Some lignite can be used as additive in drilling mud (drilling for oil and gas) as a lubricant and sealant. Young [1993] reviewed some other non-fuel applications of coals, particularly low-rank coals. They are 1) form coke from non-coking coals for use as a reductant in the metallurgical industries; 2) agricultural use of low-rank coals for production of coal-based fertilizers, soil conditioners, and humic acids; 3) special adsorbent carbons for storage of gases such as methane; and 4) production of carbon black and carbon support for making catalysts.

Carbon-based Materials Made from Coal-derived Liquids. The heavy fractions of coal tars, widely called coal tar pitches, are the raw materials for making carbon fibers and other carbon materials such as mesocarbon microbeads [Matsumura, 1989; Song and Schobert, 1993; Derbyshire et al., 1994].

The liquids and semi-liquids derived from coal extraction and liquefaction can also be used for making various carbon-based materials such as carbon fibers and graphitic materials. Kimber et al. [1981] and Zondlo et al. [1993] reported on the production of graphitic materials from carbonization of coal extracts. Kimber and Gray [1976] also noted that there are potential advantages in using coal-based coke for making carbon electrodes. Fei et al. [1994] reported on the production and properties of carbon fibers from coal-derived liquids as well as shale oils. Some lignite in California is used in an extraction process to make Montan wax, which may be used in shoe polishes, elastics, and electrical insulating [Bonskowski, 1994].

On-going Research on Production of Carbon Materials from Coal and Coal Liquids in This Laboratory

In the following section, specific examples will be provided from work in progress on carbon materials in our laboratory, including conversion of coal and pitch materials into various carbon materials.

Conversion of anthracite into graphite. Our interest in the possibility of converting anthracite into graphite was stimulated by two considerations: anthracites already contain well over 90% carbon, with aromaticities of essentially 1; and while anthracite currently sells in the range of $80 per ton, the best quality graphite materials sell for about $80 per *pound*. Our initial research was motivated by two hypotheses. First, the alignment of the large aromatic sheets presumed to exist in anthracite into the ideal graphitic structure could be facilitated by removing any residual heteroatom or aliphatic carbon atoms that might serve as covalent crosslinks "locking" the aromatic sheets into disordered structures. This, it was hypothesized, could be accomplished by reaction of anthracite with powerful hydrogen donors, such as 9,10-dihydrophenanthrene or 1,2,3,4-tetrahydro-fluoranthene prior to graphitization. Second, this process would be facilitated further if the spent donor (e.g., phenanthrene arising from 9,10-dihydrophenanthrene) was itself a graphitizable material and could therefore provide sites around which the graphitic structure could grow.

We have investigated the reactions of several Pennsylvania anthracites with hydrogen donors [Atria et al., 1993, 1994; Atria, 1995]. Co-carbonization of anthracite with a hydrogen donor, followed by high-temperature graphitization, produces a material having crystalline d-spacings in the range 0.3357–0.3361 nm, values which are quite close to the ideal value for graphite, 0.3354 nm. However, the crystalline height, L_c, of the best materials are in the range 54.7–58.8 nm, about half the value

(104.0 nm) observed in commercial graphite. As part of this work we have obtained unequivocal evidence that hydrogenation of anthracite does occur by direct reaction with hydrogen donors.

To further improve the quality of the graphitic product, we have begun an investigation of the catalytic graphitization of anthracites [Zeng et al., 1995a]. In this work, six Pennsylvania anthracites are being evaluated as feedstocks. The catalysts currently under investigation are La_2O_3, Ce_2O_3, and Gd_2O_3, mixed with anthracites in amounts up to 5%. A second aim of this present project is to reduce substantially the temperature of graphitization. We are investigating graphitization temperatures as low as 1800°C, whereas in our earlier work much of the graphitization was done at 2900°C. A very large reduction in graphitization temperature translates to a significant energy saving in the graphitization process.

Conversion of Coals into Activated Carbons. At present, the main thrust of our work is again devoted to Pennsylvania anthracites. A small collateral effort is underway on activation of Turkish low-rank coals, in conjunction with various agricultural products indigenous to Turkey.

Steam and air activation have been investigated for production of carbons from anthracites [Gergova et al., 1993a, 1993b]. The highest BET surface area obtained was 720 m^2/g [Gergova et al., 1993b]. The particle size of the anthracite is a critical parameter; the best carbon (in terms of apparent surface area) was obtained from anthracite of <1 mm particle size. Subsequent work [Gergova et al., 1995] has used an environmental scanning electron microscope (ESEM) to observe development of a porous structure in real time, even though the ESEM operates at 2 Torr, whereas normally activation is done at atmospheric pressure. In this work we also investigated air treatment of the anthracite (e.g., 3 h at 300°C) prior to steam activation. The activated anthracites produced in the latter study have a microporous structure with a significant fraction of the pores having molecular dimensions. This suggests that molecular sieve materials could be produced from Pennsylvania anthracites.

Related Studies on Anthracites. Anthracite has long been an "orphan" in coal science research. Only a tiny fraction of the coal literature is devoted to reports of work on anthracites; in consequence, little fundamental information is available on anthracite properties and structure. Recently we have begun a collaborative effort with Carbone-Lorraine North America to investigate the basic physical properties of anthracites [Zeng et al., 1995b]. Major physical properties, including density, mechanical strength, hardness, coefficient of thermal expansion, and microstructure, are being measured and correlated with chemical properties such as proximate and ultimate analyses, porosity, apparent surface area, and aromaticity. The aim is to evaluate further the potentialities of using anthracites as raw materials for the production of various carbon products.

Very limited testing of the electrical properties of Pennsylvania anthracites has shown that they are not substantially below mesocarbon microbeads in some properties affecting use in lithium batteries or other dry cells [Zeng, 1994]. We infer, from this encouraging preliminary work, that limited, but controlled, structural modification of anthracites could make them attractive candidates for electrodes in batteries.

CONCLUDING REMARKS

Despite the relatively small amount of their non-fuel use, research into efficient use of the valuable hydrocarbon resources such as coal for non-fuel applications is becoming important.

We must always bear in mind that coal is an important source of hydrocarbons. There are many ways of using the hydrocarbon resources. Burning is only one of them. Expansion of the non-fuel uses is desirable, because coal will also become more important as source of both energy and chemical feedstocks in the next century. From the viewpoints of the resource conservation and effective utilization, many of the components in coals as well as in petroleum should be converted to, or used as value-added chemicals, polymers, and carbon materials.

George A. Olah, the 1994 Nobel Prize winner, pointed out recently [1991] that "oil and gas resources under the most optimistic scenarios won't last much longer than through the next century. Coal reserves are more abundant, but are also limited. ... I suggest we should worry much more about our limited and diminishing fossil resources." James L. Adams indicated in his recent book [1991] that "oil and coal used as fuel have allowed us to work wonders, but they are too valuable as complex hydrocarbons that can be converted into all sorts of the forms (such as plastics) to be so rapidly burned in automobiles, power plants, and furnaces."

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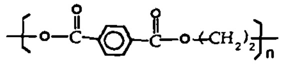
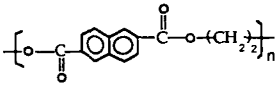
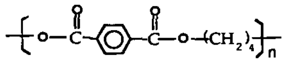
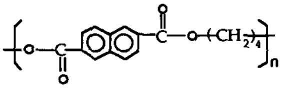
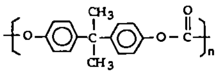
Scheme I. Structures of Some Important Aromatic Plastics Materials

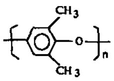

Polyethylene Terephthalate (PET) / Dacron, Mylar

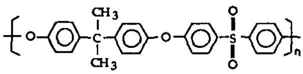

Polyethylene Naphthalate (PEN) / Teijin, Amoco

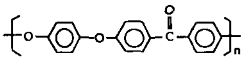

Polybutylene Terephthalate (PBT) / Valox, Celanex

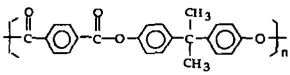

Polybutylene Naphthalate (PBN) / Teijin's PBN Resin


Polycarbonate (PC)


Polyphenylene Oxide (PPO)

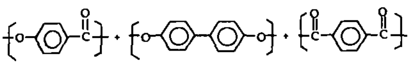

Polysulfone (PS)

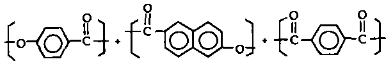

Polyphenylene Ether Ether Ketone (PEEK)

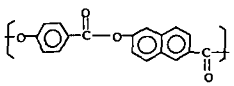

Polyarylate (PAR)

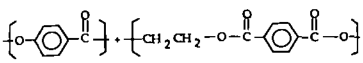
Scheme II. *Structures of Some Important Liquid Crystalline Polymers (LCPs)*

Thermotropic Polyester LCPs


Amoco's Xydar; Sumitomo's Ekonol


Hoechst Celanese's Vectra


Hoechst Celanese's LCP


Eastman Kodak's X7G; Mitsubishi's EPE; Unitika's LCP; Idemitsu's LCP

Lyotropic LCP

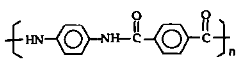

Du Pont's aramid fiber Kevlar

Table 1. World and U.S. Energy Supply and Demand

Year	Total	Petroleum	N. Gas	Coal	Nuclear	Hydropower	Other
World Total Energy Consumption / Quadrillion Btu (10^{15} Btu)							
1992	**347.5**	136.3	74.3	88.9	21.5	22.3	4.4
U.S. Energy Consumption / Quadrillion Btu							
1992	**82.42**	33.51	20.34	18.89	6.65	2.81	0.22
U.S. Energy Production / Quadrillion Btu							
1992	**66.93**	15.22	20.67	21.68	6.65	2.81	0.22
U.S. Energy Input at Electric Utilities / Quadrillion Btu							
1992	29.56	0.95	2.83	16.19	6.65	2.76	0.19

Note: According to DOE EIA, 1 quadrillion Btu is equivalent to 45 million short tons of coal, 170 million barrels of crude oil, and 1 trillion cubic feet of dry natural gas.

Table 2. Non-fuel Use of Fossil Fuels in the U.S. in 1992

Coal		Petroleum							N. Gas
Coke	Other	Petro-chemical feedstocks	Asphalt and Road Oil	Liquefied Petroleum Gases	Lubricant	Petroleum Coke	Special naphtha	Wax, etc.	Chemical feedstocks
Physical Unit / million short tons for coal; million barrels for oil; billion cubic feet for natural gas									
32.37	1.8	202	166	386	54	42	19	27	611
Energy Unit / Quadrillion Btu (10^{15} Btu)									
0.73	0.05	1.14	1.10	1.35	0.33	0.25	0.10	0.16	0.63

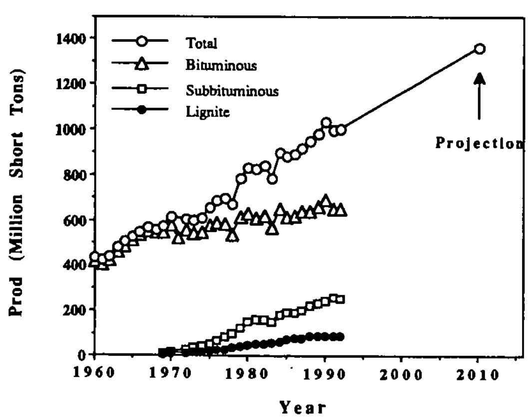


Figure 1. Production of coal by type in the U.S. during 1960-1992 (1 short ton = 0.907 metric ton).

Table 3. U.S. Coal Production and Consumption

Coal Supply and Demand / million short tons					
Year	Production	Consumption	Export	Import	Others and losses
1992	997.545	892.421	102.516	3.803	9.407

Coal Consumption by Sectors / million short tons					
Year	Electric Utilities	Coke Plants	Other Industrial	Residential and Commercial	Total consum.
1992	779.860	32.366	74.042	6.153	892.421

Note: 1 short ton = 907.184 kg = 2000 pounds = 0.907 metric ton

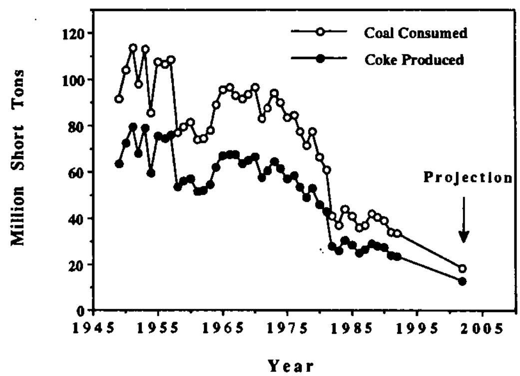


Figure 2. U.S. metallurgical coke production during 1949-1992

Table 4. U.S. Coal Consumption at Manufacturing Plants by Standard Industrial Classification Code (Thousand Short Tons)

SIC Code		Jan-March 1993	Apr-June 1993	July-Sept 1993	Oct-Dec 1993	U.S. Total
20	Food and kindred products	2264	1568	1491	2479	7802
21	Tobacco products	184	156	154	154	648
22	Textile mill products	370	313	258	334	1275
24	Lumber and wood products	27	29	23	30	109
25	Furniture and fixtures	35	18	16	32	101
26	Paper and allied products	3302	2918	2946	3270	12436
28	Chemicals, allied products	3490	3079	3044	3338	12951
29	Petroleum and coal products[1]	1760	1832	1695	1963	7250
30	Rubber, misc. plastics products	78	67	56	64	265
32	Stone, clay, glass products	2781	3170	3329	3478	12758
33	Primary metal industries[2]	1623	1833	1700	1872	7028
34	Fabricated metal products	113	59	33	80	285
35	Machinery, except electric	180	84	48	121	433
36	Electric, electronic equipment	89	59	29	68	245
XX	Other manufacturing industries (SIC: 23, 27, 31, 37, 38, 39)	w	w	w	w	w
	U.S. Total	17175	15705	15268	17931	66079

1) Includes coal gasification projects.

2) Excluding coke plants. w Withheld by DOE to avoid disclosure of individual company data.